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Ground and excited state exciton spectra from GaN grown by molecular-beam epitaxy

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The emission and reflection spectra of GaN have been investigated in the intrinsic region and the data have been interpreted in terms of the wurtzite crystal band structure. Three intrinsic exciton transitions have been observed, one associated with each of the valence bands. Exciton excited states associated with the two top valence bands were also observed. The exciton binding energies, the band-gap energies, and the exciton Bohr radii are all reported along with the dielectric constant and the spin-orbit and crystal-field parameters for GaN. © 1996 American Institute of Physics. [S0021-8979(96)01213-3]

Interest in wide band-gap materials has been increasing over the past few years. The main catalyst driving the renewed interest is the potential for high-temperature electronics, as well as the potential for short wavelength display diodes and lasers. One promising wide band-gap material possessing the properties required for the above applications is GaN. This material has been investigated for a number of years and the results of these investigations have been published in several reviews.¹⁻⁸ The equilibrium crystal structure for GaN is the wurtzite structure. In high quality material, optical characterization will reveal much information pertinent to the energy band structure of the material. In GaN, one assumes that the bottom of the conduction band is predominantly formed from the *s* levels of Ga and the upper valence band states are formed from the *p* levels of N. The upper valence band states are constructed out of appropriate linear combinations of products of $p_x p_y$, p_z —like orbitals with spin functions. In the absence of both spin-orbit and crystalline field effects, these states are degenerate. The crystal field of the wurtzite lattice partially removes the degeneracy, separating the p_z orbital from the p_x and p_y orbitals. The $p_x p_y$ band is further split by spin-orbit coupling. If one assumes an approximately spherical potential in the neighborhood of the N atoms, the higher energy of the two spin states is the one in which the electron spin and the orbital angular momentum are parallel. This result is anticipated also from the atomic spin-orbit splitting, in which the $P_{3/2}$ state is known to have a greater energy than the $P_{1/2}$ state.

The contributions of spin-orbit interaction and the crystal-field perturbation to the experimentally observable

splittings, $E_{1,2}$ and $E_{2,3}$, have been calculated in various linear combination of atomic orbitals (LCAOs) approximations by several investigators.⁹⁻¹⁴ In a treatment in which the wurtzite energy levels are treated as a perturbation of those in zinc blende structure, Hopfield¹⁵ has derived the relations

$$E_1 = 0,$$

$$E_2 = -\frac{\delta + \Delta}{2} + \sqrt{\left[\left(\frac{\delta + \Delta}{2}\right)^2 - \frac{2}{3}\delta\Delta\right]},$$

$$E_3 = -\frac{\delta + \Delta}{2} - \sqrt{\left[\left(\frac{\delta + \Delta}{2}\right)^2 - \frac{2}{3}\delta\Delta\right]},$$

where Δ and δ represent the contributions of uniaxial field and spin-orbit interaction, respectively, to the splittings $E_{1,2}$ and $E_{2,3}$. The band separations and band symmetries for the wurtzite structure are given in Fig. 1. The optical transition $\Gamma_7 \rightarrow \Gamma_9$ is allowed for $E \perp C$, where E is the electric-field vector and C is the C axis of the crystal. The optical transitions $\Gamma_7 \rightarrow \Gamma_7$ are allowed for both $E \perp C$ and $E \parallel C$.

One problem that has slowed research on GaN is the lack of consistently high quality material. The techniques most recently used to grow GaN are molecular-beam epitaxy (MBE) and metalorganic chemical vapor deposition (MOCVD). The majority of material has been grown on sapphire substrates with some effort on Si, SiC, and GaAs. The lattice mismatch between the substrates and GaN is substantial; this leads to strain-induced defects and dislocations. The general consensus to date has been that the highest quality epitaxial GaN has been grown by MOCVD. It is the purpose of this article to show that very high quality GaN can be grown by MBE. To support this conclusion, excited states of the *A*- and *B*-band excitons are reported, to the best of our knowledge, for the first time, from which the exciton binding energies are determined. The dielectric constant can then be derived from the reduced mass of the exciton and the exciton binding energy. Definitive values are given for the *A* and *B*

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WURTZITE

FIG. 1. Band separations and band symmetries for the wurtzite lattice.

band-gap energies. The exciton Bohr radii for the A- and B-band excitons are derived from the dielectric constant and the reduced mass. In addition, values are given for the spin-orbit and crystal-field parameters obtained using the quasi-cubic model.

The GaN sample used in this experiment was grown by MBE on a sapphire substrate. The sample was high resistivity, preventing carrier mobility measurements; as a result, characterization was accomplished by optical techniques. The sample thickness was 6 μm . The optical transitions from the sample were studied in photoluminescence (PL) and reflection. The PL was excited with a He-Cd laser. The reflection source was a xenon lamp. The reflection was measured at approximately 15° off normal incidence; this was necessary because of the dewar arrangement and the collection optics. The measurements were made at 2 K with the sample immersed in liquid He. The spectra were analyzed with a high-resolution 4 m spectrometer equipped with an RCA C31034A photomultiplier tube for detection.

The PL spectra for the GaN sample are shown in Fig. 2. The ground state exciton transitions associated with the A- and B-bands are dominant; also seen are the $n=2$ excited state A exciton and the $n=2$ and 3 excited state B excitons. Assuming hydrogenlike excitons, the A-exciton binding energy is 0.020 eV and the B-exciton binding energy is 0.022 eV. Adding the A-exciton binding energy to the A-exciton transition energy results in an A band gap of 3.5031 eV. Likewise, adding the B-exciton binding energy to the

FIG. 2. Photoluminescence spectra for GaN 2⁰ K.

FIG. 3. Reflection spectra from the GaN sample shown in Fig. 2.

B-exciton transition energy gives a B band gap of 3.5116 eV. The exciton associated with the C exciton is not seen in emission, however, it can be seen in reflection as shown in Fig. 3. In this experiment we are doing straight reflection, however it is off normal incidence by approximately 15° , as noted before. The minimum in the A and B reflection peaks is shifted to higher energy from the A and B emission peaks by approximately 7 meV. The emission peaks occur at the oscillator and therefore give the correct transition energy. The exciton associated with the C band does not show in emission, therefore we have made a 7 meV correction to the C-band reflection minimum to be consistent with the A- and B-band reflection minima. This leaves some uncertainty as to the exact position of the C-band oscillator. With the correction added, the C-band exciton transition energy is 3.518 eV. We feel that this is more accurate than applying a Kramers-Kronig analysis since the applicability of the Kramers-Kronig analysis to reflection oscillators that are closely spaced is questionable.¹⁴ An excited state of the C-band exciton was not observed; as a result the C-band exciton binding energy could not be determined; thus, the C band gap is also not known.

Considering the quasi-cubic model of Hopfield,¹⁵ $E_{1,2}$ is the difference in energy between the A and B band gaps deduced from the ground and excited state exciton transition energies. The term $E_{2,3}$ is the energy difference between the B and C exciton transition energies. This difference has been measured from the reflection spectra since the C-exciton emission was not observed. The energies of the reflection minima from Fig. 3 were taken as the exciton transition energies, realizing that these are probably not the energy positions of the oscillators. Since we are concerned only with the energy difference, this choice will allow one to obtain a reasonably accurate value for $E_{2,3}$. If we assume that the B- and C-band excitons have the same binding energies, then the difference in energy between the reflection minima will also be the difference in energy between the B and C band gaps. This has been observed in other materials. For example, Litton *et al.*¹⁶ showed that the A and B excitons in CdS had the same binding energies. Thomas¹⁷ reported that the binding energies of the A, B, and C excitons in ZnO were within 1 meV of each other. Substituting the $E_{1,2}$ and $E_{2,3}$ values into the quasi-cubic model, the spin-orbit and crystal-field param-

TABLE I. Some parameters pertinent to GaN.

Parameters	Values	Measured	Derived
A exciton			
Ground state energy	3.4831 eV	X	
$n=2$ energy	3.4982 eV	X	
Exciton binding energy	0.02 eV		X
Band-gap energy	3.5031 ± 0.0005 eV		X
Effective mass	$0.129 m_0$		X
Bohr radius	36 Å		X
B exciton			
Ground state energy	3.4896 eV	X	
$n=2$ energy	3.5067 eV	X	
$n=3$ energy	3.5093 eV	X	
Exciton binding energy	0.022 eV		X
Band-gap energy	3.5116 ± 0.0005 eV		X
Effective mass	$0.143 m_0$		X
Bohr radius	32.5 Å		X
C exciton			
Ground state energy	3.518 eV		X
$E_{AB}, \Gamma_q \Gamma_7$	0.0085 eV		X
$E_{BC}, \Gamma_7 \Gamma_7$	0.025 eV		X
Dielectric constant	$\epsilon=9.3$		X
Spin-orbit parameter	0.0173 eV		X
Crystal-field parameter	0.0247 eV		X

eters (δ and Δ , respectively) can be obtained. Assuming $\delta < \Delta$, the spin-orbit parameter is 17.3 meV while the crystal-field parameter is found to be 24.7 meV. One would expect the spin-orbit splitting to be small due to the small atomic number of N; thus the calculated parameters appear to be reasonable. From the binding energy of the exciton and the reduced mass, the dielectric constant for GaN is obtained. Using an electron mass $m_e=0.19$ and a hole mass $m_h=0.4$,¹⁸ a reduced mass $m^*=0.129 m_0$ is obtained. Combining this with the A-exciton binding energy, a dielectric constant $\epsilon=9.3$ is derived. Using the expression

$$a = a_0 \frac{\epsilon}{\mu}$$

the Bohr radius of the A and B excitons were determined to be 36 and 32.5 Å, respectively. The pertinent parameters that have been measured and derived from the exciton spectra of GaN are compiled in Table I. The A, B, and C exciton transitions that we have observed agree well with the same transitions observed by Dingle *et al.*¹⁹ and by Shan *et al.*²⁰

This article reports, to the best of our knowledge, the first experimental observation of exciton binding energies and band-gap energies for the A and B bands in GaN crystals. The dielectric constant was derived from the measured exciton binding energy and the literature values of the carrier masses. The Bohr radii were derived from the dielectric constant value and the exciton reduced mass.

One cannot conclude from these measurements that there is no residual strain in the GaN layer which may result from the lattice mismatch as well as a mismatch of the thermal expansion coefficients. Much of the characterization of GaN crystals has been accomplished by optical techniques. The results of this characterization, such as exciton structure, allow one to compare crystal quality between samples. Residual strain effects will also occur in crystals grown by MOCVD. Strain can result in shifts of the transition energies as well as changes in the energy separations between the A, B, and C excitons. Comparing the characterization results between samples allow one to conclude that the quality of the present MBE grown GaN layer compares very well with the best MOCVD grown layers.

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